Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Earth and Planetary Science 7 (2013) 264 – 267

Procedia
Earth and Planetary Science

Water Rock Interaction [WRI 14]

Effect of zeolite formation on borosilicate glass dissolution kinetics

Maxime Fournier*, Pierre Frugier, Stéphane Gin

CEA, DEN-Marcoule, F30207, Bagnols-sur-Cèze, France

Abstract

This study is a preliminary work on the description and the modeling of physico-chemical mechanisms potentially causing nuclear glass alteration to accelerate, as observed under experimental specific conditions. A better understanding of the mechanisms of alteration resumption, linked to the precipitation of zeolite, is necessary to model these phenomena. Leaching tests of a nuclear borosilicate glass show guidelines for designing experiments that promote alteration resumption and evidence the role of developed crystalline surfaces and aluminum on nucleation kinetics of zeolites.

Keywords: nuclear glass; kinetics; alteration; resumption; zeolites.

1. Introduction

In the framework of studies on the long-term behavior of the vitrified waste, in order to ensure glass lifetime, we rely on its resistance to leaching in a broad range of conditions. If the main regimes of glass alteration are now well known [1], alteration resumptions is a phenomenon that requires further investigation. For most of glasses of nuclear interest, these phenomena have never been observed in laboratory experiments at $pH < 10$ and $T < 90°C$ [2] and are systematically associated with the precipitation of zeolites-type alumino-silicate minerals. These minerals are also found to result from the alteration of ancient basaltic glasses [3].

Zeolites precipitation and its effect on borosilicate glasses alteration highly depend on:

- glass composition, including aluminum content [4];
- solution composition, especially alkalinity [5, 6] and pH [7];
- temperature.

* Corresponding author. Tel.: +33 466797710; fax: +33 466796612
E-mail address: maxime.fournier@cea.fr.

doi:10.1016/j.proeps.2013.03.085

Alteration resumptions may occur after several years of leaching, but more accessible time scales are required when it comes to identify the mechanism that controls zeolites precipitation. Therefore, the conditions for exploratory experiments have to be chosen in order to favor their formation. A special attention was paid to the influence of secondary nucleation.

2. Material and methods

The glass selected for this study is used for the vitrification of intermediate level waste and is planned to be disposed in a cementitious environment (Table 1) [8]. Glass was crushed (20-40 microns, BET specific surface area of 1 595 $cm^2.g^{-1}$) before being leached in static mode and inert atmosphere, without (first experiment) or with (second set of experiments) addition of analcime ($NaAlSi_2O_6$-H_2O) at the beginning of the experiment.

Experimental conditions are as follows:

- high glass-surface-area-to-solution-volume ratio (S/V) of 40 cm^{-1} and 200 cm^{-1} in order to quickly reach 'saturation' conditions;
- relatively high-end temperatures (50°C and 90°C) compared to those expected in storage;
- highly alkaline medium (0.2 M NaOH solution giving a pH of 12.4 ± 0.2 at 50°C and 11.4 ± 0.2 at 90°C) *i.e.* a pH close to what is expected for a cementitious solution. pH is maintained at its initial value by regular additions of appropriate volumes of 5 N NaOH (Prolabo AVS Titrinorm).

During leaching tests, regular sampling of 0.5 mL were taken and analyzed by ICP-AES. Samples of glass powder were regularly retrieved and characterized by SEM and Energy Dispersive Spectroscopy. Once glass is fully altered, neo-formed zeolites are identified by XRD.

Altered glass percentage (AG%) was calculated from the boron concentration in solution and then translated into equivalent alteration thickness taking into account S/V variations with time [9]. Boron is known to be a mobile element (not retained in secondary phases once released from the glass).

Table 1. Composition of the CSD-B glass expressed in oxide weight percent.

Oxide	SiO_2	B_2O_3	Na_2O	Al_2O_3	Li_2O	CaO	Fe_2O_3	ZrO_2	NiO	MoO_3
wt%	50.32	14.44	12.58	8.70	2.17	3.10	2.84	1.99	0.33	0.69
Oxide	CoO	P_2O_5	SO_3	BaO	Ce_2O_3	MnO_2	Nd_2O_3	RuO_2	Cr_2O_3	La_2O_3
wt%	0.27	0.42	0.19	0.36	0.75	0.19	0.41	0.12	0.07	0.06

3. Results and discussion

3.1. Influence of environmental conditions

At 90°C, pH 11.4 and S/V = 40 cm^{-1}, the glass is completely altered after one week of leaching (Fig. 1.a). Aluminum concentration in solution increases until a threshold value of about 230 $mg.L^{-1}$ is reached and then decreases. Unlike boron, aluminum is consumed by zeolite formation. Thus, aluminum increasing concentration indicates that zeolites precipitation, although observed after 31 hours (SEM, Fig. 1.a), is slower than glass dissolution, and estimated at 0.48 ± 0.02 $\mu m.j^{-1}$ between 0 and 4 days. Conversely, rapid decrease in aluminum concentration after 3 days shows a massive precipitation of zeolites causing a significant acceleration of glass alteration (at a minimum of 1.3 $\mu m.j^{-1}$) which brings the aluminum and the silicon necessary for the growth of minerals identified by XRD (Fig. 1.b) as zeolite P $(NaAlO_2)_7(SiO_2)_9$.

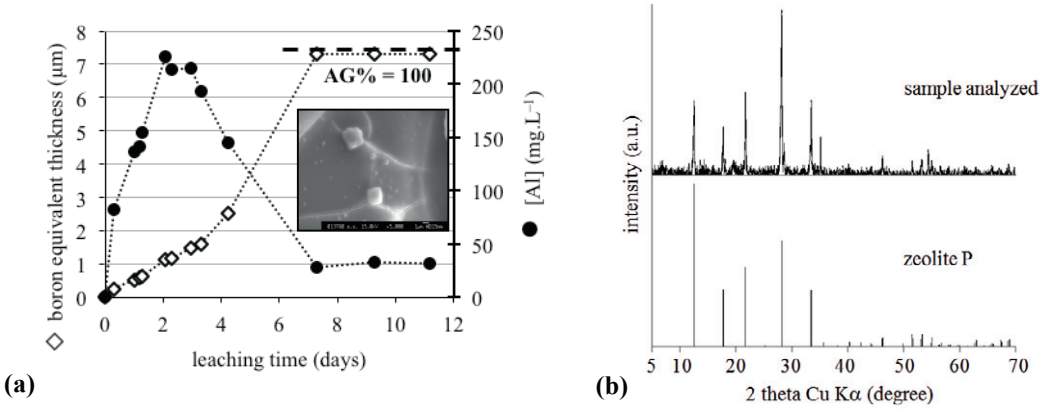

Fig. 1. (a) Boron equivalent thickness and aluminum concentration versus time at 90°C, 40 cm^{-1} (photograph: first zeolites are observable by SEM after 31 h); (b) Correlation between XRD zeolite P and obtained diffractogram.

Zeolites nucleation and growth processes constantly increase the surface of these minerals during the reaction. This parameter, which may control the mass transfer, particularly via secondary nucleation, could be the cause for the trend change initiated at 3 days. This hypothesis is tested by the following experiments.

3.2. Influence of crystalline surface

Natural analcime crystals (Alfa Aesar) have been crushed (40-125 µm, BET specific surface of 1 386 $cm^2.g^{-1}$) and added to leaching tests with zeolite-surface-area-to-glass-surface-area (Sz/Sg) ratios between 0 (reference) and 1/3.

Existence of secondary nucleation would result in a faster alteration of glass in an initially containing zeolites media. However, the difference between equivalent thicknesses at 50°C, S/V = 200 cm^{-1} is insignificant (Fig. 2.a). This small difference could be explained by an increase of primary heterogeneous nucleation surface, represented by the dashed curve obtained by adding zeolites and glass specific surface areas (the 'global S/V' of the system, including glass and zeolites, is equal to (Sg+Sz)/V = 266 cm^{-1}).

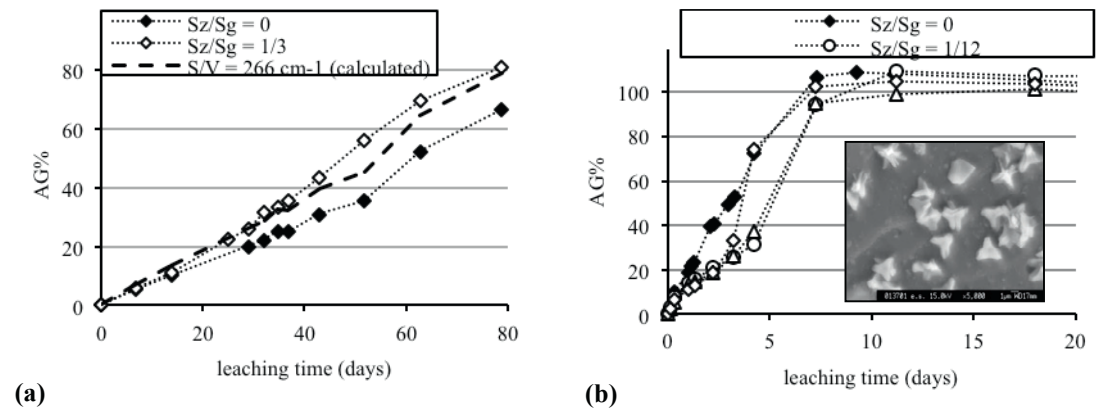

Fig. 2. (a) altered glass percentage at 50°C, S/V = 200 cm^{-1} and (b) at 90°C, S/V = 40 cm^{-1} for various Sz/Sg ratios versus time (SEM reveals neo-formed crystals on initially introduced analcime grains after 10 days).

These results are confirmed by tests at 90°C, S/V = 40 cm^{-1} (Fig. 2.b) in which AG% undergo similar changes regardless of the initial surface of zeolites (Sz/Sg = 0, 1/12, 1/6 or 1/3). In all reactors, the evolution of aluminum concentration is the same as that shown in Fig. 1.a. Note that it has been checked that analcime added to the medium in absence of glass does not induce significant changes.

Surface of analcime initially added does not seem to control the kinetics of zeolite precipitation. However, Fig. 1.b suggests that, as opposed to what was observed by Depierre [10], the neoformed crystals may not have the same chemical composition than the analcime initially introduced: zeolite P has a Si/Al ratio close to 1 instead of 2 for analcime. This could explain the poor effect of analcime surface on glass alteration. New experiments will investigate this issue: indeed, if the amount of zeolite precipitation rate depends on available surface, then setting it at a controlled value would be a valuable tool for studying slower kinetics.

4. Conclusion

Leaching tests conducted in this study show that a few days are sufficient to observe alteration resumptions under favorable conditions. Tests carried out at imposed pH were successful: in addition to the increase of the alteration rate, the invariance of this parameter eliminates the pH dependence of studied chemical mechanisms.

Adding an initial amount of analcime had no effect on glass alteration. Therefore, either the crystalline surface does not control the precipitation of zeolites or the nature/amount of the zeolite was not suitable. Finding the limiting mechanism for zeolite precipitation requires further experiments.

Acknowledgements

This paper results from a partnership between CEA and AREVA.

References

[1] Frugier P, Gin S, Minet Y, Chave T, Bonin B, Godon N, et al. SON68 nuclear glass dissolution kinetics: Current state of knowledge and basis of the new GRAAL model. *J Nucl Mater* 2008; **380**: 8-21.

[2] Ribet S, Muller IS, Pegg IL, Gin S, Frugier P. Compositional effects on the long-term durability of nuclear waste glasses: A statistical approach. *Mater Res Soc Symp Proc* 2004; **824**: 309-314

[3] Le Gal X, Crovisier JL, Gauthier-Lafaye F, Honnorez J, Grambow B. Meteoritic alteration of Icelandic volcanic glass: long-term changes in the mechanism. *CR Acad Sci, Ser IIa: Sci Terre Planets* 1999; **329**: 175-181

[4] Strachan DM, Croak TL. Compositional effects on long term dissolution of borosilicate glass. *J Non-Crys Solids* 2000; **272**: 22-33.

[5] Vigil de la Villa R, Cuevas J, Ramírez S, Leguey S. Zeolite formation during the alkaline reaction of bentonite. *Eur J Mineral* 2001; **13**: 635-644.

[6] Ribet S, Gin S. Role of neoformed phases on the mechanisms controlling the resumption of SON68 glass alteration in alkaline media. *J Nucl Mater* 2004; **324**: 152-164.

[7] Gin S, Mestre JP. SON 68 nuclear glass alteration kinetics between pH 7 and pH 11.5. *J Nucl Mater* 2001; **295**: 83-96.

[8] ANDRA. *Dossier 2005: Andra research on the geological disposal of hight-level long-lived radioactive waste - Results and perspectives*. Andra 265VA; 2006.

[9] Chave T, Frugier P, Gin S, Ayral A. Glass-water interphase reactivity with calcium rich solution. *Geochim Cosmochim Acta* 2011; **75**: 4125-4139.

[10] Depierre S. Etude des mécanismes d'altération du verre par des eaux cimentaires. *PhD thesis, University of Montpellier*, France.